Organoboron Substituent Effects in EPR/ENDOR Spectroscopy. Radical Ions with B–C and B–N Bonds

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The consequences of R_3B coordination ($R = CH_3, C_2H_5, C_6H_{11}$) to nitrogen-containing anion radicals and of Mes_2B substitution ($Mes =$ mesityl, C_9H_{11}) at C or N π centres of radical ions have been studied for a series of closely related carbo- and hetero-cyclic π systems by EPR/ENDOR spectroscopy. Examples include the anion radicals of dinuclear R_3B coordination compounds with pyrazine and 4,4′-bipyridine, *para*-diboryl substituted benzene and biphenyl radical anions and the correspondingly substituted 1,4-dihydropyrazine and 1,1′-dihydro-4,4′-bipyridine radical cations. Whereas the perturbation of spin distribution is most pronounced for the dimesitylboryl-substituted homoaromatic anions, the isoelectronic cations of the non-aromatic Mes_2B-substituted dihydroheterocycles exhibit a substantial decrease of the heteronuclear (^{11}B, ^{14}N) EPR/ENDOR coupling constants owing to a considerable degree of B/N π bonding. MO/McLachlan perturbation calculations suggest that both the orbital overlap and the electronegativity differences contribute to the observed effects.

One of the classical methods to evaluate substituent effects in organic chemistry is to study the spin distribution in correspondingly substituted π radical ions.[1] This approach is not confined to all-carbon π systems, it can be extended *e.g.* to N amine or imine centres in heterocycles from which covalent or coordinative bonds can originate.[2,3]

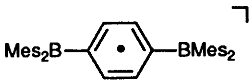
There have been only very few studies on the EPR substituent effects of boron-containing groups,[2–6] of diorganoboryl substituents[2,5] or Lewis-acidic triorganoboranes coordinated to a nitrogen lone pair.[3,6] This situation is all the more unfortunate since boron–nitrogen bonds, either in the form of Lewis acid/Lewis base interactions $\geqslant B \leftarrow N \leqslant$ or as polar multiple bonds $>\overset{-}{B}=\overset{+}{N}<$ (isoelectronic with $>C=C<$) in aminoboranes[7] or borazines are continuing to play an important role in the elementary understanding of chemical bonding.[8]

In this work we present comprehensive EPR/ENDOR results on three kinds of radical ions which should permit an evaluation of the substituent effects exerted by organoborane groups under different circumstances.

First, the rather facile reduction of *para*-bis(dimesitylboryl)-substituted aromatics[9] allowed us to study the persistent radical anions **1** and **2** which are members of two-step reversible redox systems[9] which are 'inversely' related[5] to *p*-phenylenediamine and benzidine radical cations.

Isoelectronic[10] to the anions **1** and **2** are the radical cations **3** and **4** of electron-rich *N,N′*-bis(dimesitylboryl)-substituted dihydroheteroaromatics, the neutral forms of which may be described as 'inorganic analogues' of *p*-quinodimethanes and 4,4′-biphenyl-4,4′-diylbis(diorganomethyl) compounds (*cf.* Chichibabin's hydrocarbon).[10a] The dimesitylboryl group is known to prevent intermolecular aggregation by effectively protecting the empty p_z orbital at boron and thus restricting the coordination number to three.[9,11]

Finally, singly reduced heteroaromatics such as pyrazine or 4,4′-bipyridine anion radicals are known to form strong adducts **5b** and **6** with two molecules of triethylborane to yield isoelectronic analogues of dialkylpyrazinium and methyl viologen radical cations;[6] in this paper we finally clarify the sometimes differently[3,6,12] presented nature of such species by describing the complete EPR/ENDOR analysis of the *anionic* trimethylborane analogue **5a** and by comparing these results with the data for *cationic* species such as **3**. The difference between the radical cations **3** or **4** and radical anions such as **5** or **6** is two carbanions R^-; the relatively easy exchange of carbanions between coordinatively unsaturated organometallic radical species has been demonstrated recently.[13]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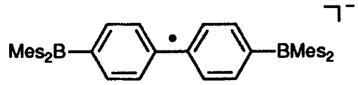
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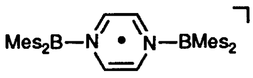
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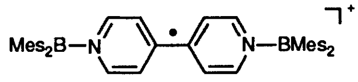
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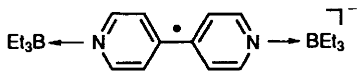
5a; $R = CH_3$
5b; $R = C_2H_5$
5c; $R = C_6H_{11}$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Experimental

Materials.—Syntheses of the neutral precursors of the radical ions studied in this work have been described.[9,10a] Trimethylborane was prepared according to literature procedures.[14,15] The yellow adducts of pyrazine (Pz) with two BMe_3, BEt_3 and $B(c\text{-}Hex_3)$ molecules were used for radical generation *in situ* (see below); neutral compounds $(Pz)[BR_3]_2$ were prepared as air-sensitive oils ($R =$ Me, Et) or crystals ($R =$ c-Hex) by adding the components in a 1:2 molar ratio in toluene. The precursor of **6**, $(Bp)[BR_3]_2$ (Bp = 4,4′-bipyridine), was obtained in an analogous fashion.

Sample Preparation.—Anion radicals $[Mes_2B(\pi)BMes_2]^{\bullet -}$ **1** and **2** were generated in sealed glass tubes from neutral precursors by reduction with potassium in tetrahydrofuran (THF) at room temperature. Cation radicals $[Mes_2B(N\text{-}\pi\text{-}N)BMes_2]^{\bullet +}$ were obtained from neutral precursors by oxidation in dichloromethane with iodine–potassium perchlorate at 295 K (**3**) or with $AlCl_3$ at 235 K (**4**). Bis(triorganoboron) complexes **5** and **6** of heterocyclic anion radicals were obtained at room temperature from neutral precursor adducts by reduction with potassium metal in THF.

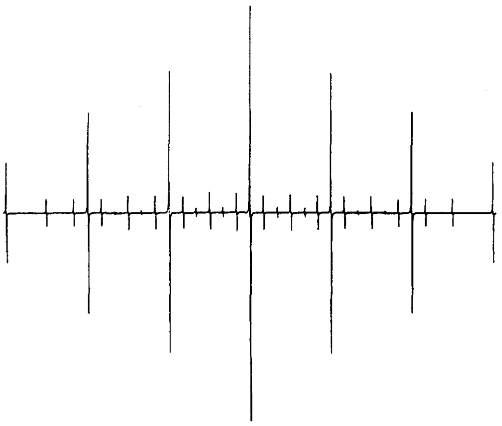


Fig. 1 EPR stick spectrum for the hyperfine coupling of one unpaired electron with two equivalent boron nuclei in natural abundance (for details see the text)

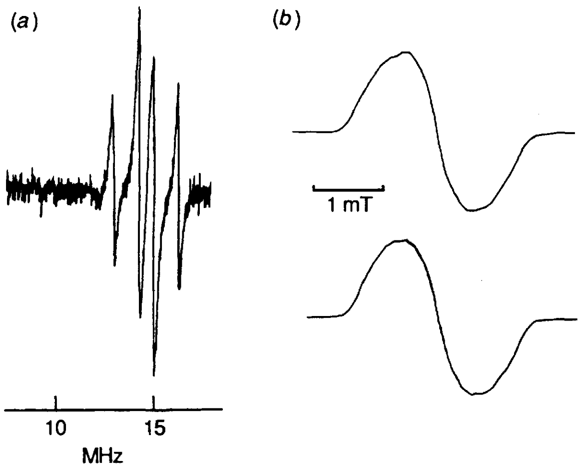


Fig. 2 ENDOR spectrum of anion radical **1** in THF at 180 K (*a*); EPR signal and computer simulation with the data from Table 1 (*b*)

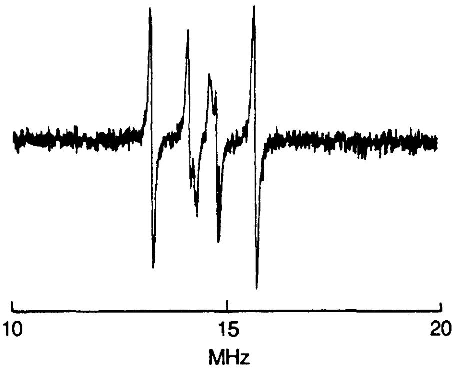


Fig. 3 ENDOR spectrum of anion radical **2** in THF at 200 K

Instrumentation.—EPR and ENDOR spectra were recorded in the X band on a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter and a HP 5350B microwave counter. Typical ENDOR parameters were 400 mW rf power, 100 mW mw power, 12.5 kHz field modulation and 70 kHz fm depth. NMR spectra were taken on a Bruker WP 60 spectrometer, cyclic voltammetry was carried out in 1,2-dichloroethane 0.1 mol dm^{-3} Bu_4NClO_4 using a three-electrode configuration (GCE, SCE, Pt) and a PAR 273/175 potentiostat and function generator.

HMO/McLachlan Calculations.—Calculations were performed with standard programs,[16,17] using the following parameters: McLachlan parameter $\lambda = 1.2$;[1,17] Coulomb integral parameters $h_B = -1.0$ and $h_N = +1.0$;[1,16] overlap integral parameters were varied between 0.5 and 1.0 (k_{BC}) and between 0.5 and 1.5 (k_{BN}).

Results

$[Mes_2B(\pi)BMes_2]^{\cdot-}$.—Due to the large number of theoretical lines ($>10^5$) from ^{1}H, ^{14}N and, in particular, ^{11}B and ^{10}B hyperfine coupling, the EPR spectra of the chemically generated anion radicals **1** and **2** are virtually non-resolved (*cf.* insert in Fig. 2). Naturally occurring boron consists of two isotopes, ^{10}B ($I = 3$, 19.8%, $A_{iso} = 24.141$ mT) and ^{11}B ($I = 3/2$, 80.2%, $A_{iso} = 72.082$ mT). Two equivalent boron nuclei should give rise to three sub-spectra containing the isotope combinations ^{11}B/^{11}B (64.3%, septet), ^{11}B/^{10}B (31.8%, quartet of septets), and ^{10}B/^{10}B (3.9%, tridecet). A computer-generated stick spectrum is shown in Fig. 1.

ENDOR studies of **1** and **2** at low temperature in fluid solution revealed only ^{1}H hyperfine coupling (Figs. 2 and 3, Table 1); coupling with the boron isotopes ^{10}B and ^{11}B was not ENDOR-detectable under those conditions and had to be estimated by EPR computer simulations (Fig. 2). Reasons for the absence of ^{10}B and ^{11}B ENDOR signals could be the high spin population (see below) and anisotropic coordination of boron in triarylborane anion radicals;[18,19] a theoretical treatment was provided by Plato *et al.*[20]

The ENDOR spectra exhibit rather small ^{1}H hyperfine coupling in the benzene (**1**) and biphenyl π systems (**2**). It was pointed out previously that the value of 0.119 mT for the phenyl protons in **1** is almost as low as the ^{1}H coupling (0.112 mT) in 1,4-dinitrobenzene radical anion.[5] Similarly, the considerable spin delocalization to the boryl π acceptor sites of the biphenyl derivative **2** is responsible for a largest ^{1}H hyperfine splitting of only 0.085 mT (Fig. 3). Because of the peak intensity and the HMO/McLachlan calculation results (see below) we assign this coupling to both chemically inequivalent kinds of ring protons 2,6,2′,6′-H and 3,5,3′,5′-H. Remarkably, the ^{1}H-NMR chemical shifts of these protons are also identical in the neutral precursor compound.[9] The remaining two very small hyperfine splittings in the anion radical **2** are due to protons in the mesityl substituents (*o*-methyl, *m*-CH or *p*-methyl); an unambiguous assignment is not possible without selective deuteriation, since the sign and magnitude of hyperfine couplings of such tilted aryl substituents depend very much on the tilt angle.[21]

While the ^{1}H-ENDOR data of electrochemically stable[9] **1** and **2** point to substantial spin delocalization from the central aromatic π system to the dimesitylboryl substituents in the *para* position, the ^{11}B coupling constants for *two* boron nuclei as estimated from computer simulated spectra (see Fig. 2) have an order of magnitude (0.2–0.3 mT) which is in agreement with the *ca.* 0.8 mT observed for *one* ^{11}B centre in more localized triarylmonoborane radical anions.[18,19]

HMO-McLachlan calculations of π spin populations were carried out for **1** and **2**, incorporating boron π centres with the Coulomb integral parameter $h_B = -1.0$[16] but neglecting the (tilted) mesityl groups. Variation of the boron–carbon overlap integral parameter k_{BC} (Fig. 4) showed a degeneracy of spin populations ρ (and of McConnell-calculated coupling constants $a_H = Q \cdot \rho$, $Q = 2.3$ mT)[1] at the two chemically different biphenyl CH centres of **2** for k_{BC} *ca.* 0.75. This relative 'calibration' of k_{BC} is supported by the calculated absolute values ($Q = 2.3$ mT)[1] of 0.09 mT for **2** and 0.14 mT for **1** (Fig. 4) which agree quite well with the experimental ring proton coupling constants of 0.085 mT (**2**) and 0.119 mT (**1**) (Table 1). The thus validated calculation yields π spin populations of 0.186 and 0.116 for each boron centre in **1** and **2**, respectively, suggesting a

Table 1 Coupling constants and g factors of borane radical ions from EPR/ENDOR spectroscopy (1 mT = 28 MHz)

Radical ion (temperature)	$a(^1H)$ Central π system	$a(^1H)$ Substituents	$a(^{11}B)$	$a(^{14}N)$	g
1 (180 K)	0.119	0.029	0.3[a]	—	2.0024
2 (200 K)	0.085 (2-H) 0.085 (3-H)	0.023 0.014	0.2[a]	—	2.0027
3 (190 K)	0.315	0.019	0.081	0.42[b]	2.0029
4 (220 K)	0.083 (3-H) 0.225 (2-H)	0.011	0.016	0.15[b]	2.0030
5a (305 K)	0.254	0.016[c]	0.237	0.803	2.0035
5b (220 K)	0.261	0.008[d]	0.259[e]	0.802	2.0035
5c (300 K)[f]	0.24	n.o.	0.24	0.805	2.0034
6 (200 K)	0.078 (2-H) 0.203 (3-H)	0.004[d]	0.138[g]	0.420	2.0032

[a] Estimated from computer-simulated EPR spectra, using ^1H ENDOR data. [b] Estimated from computer-simulated EPR spectra, using ^1H and ^{11}B ENDOR data. [c] 18 H. [d] CH_2 protons. [e] $a(^{10}B)$ = 0.087 mT (ref. 6). [f] From EPR measurements. [g] $a(^{10}B)$ = 0.046 mT (ref. 6).

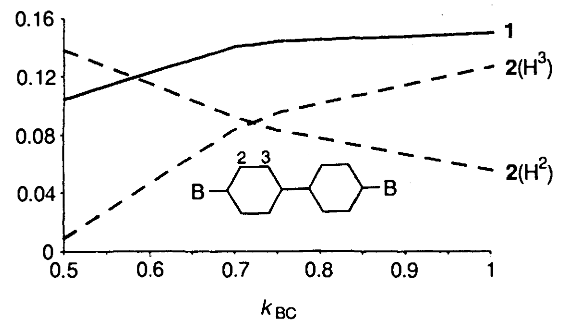


Fig. 4 Correlation of HMO/McLachlan-calculated ^1H coupling constants (Q_{CH} = 2.3 mT) with the overlap integral parameter k_{BC} for π systems **1** (——) and **2** (– – – –) (h_B = −1.0; mesityl groups are neglected)

sizeable contribution from the 'mixed valence' resonance form as indicated below.[9]

$$[B^{II}–(\pi)–B^{III}]^{\bullet -} \longleftrightarrow [B^{III}–(\pi)–B^{II}]^{\bullet -}$$

$[Mes_2B(N–\pi–N)BMes_2]^{\bullet +}$.—Formal substitution of the external C=C bonds in 7,7,8,8-tetraaryl-*p*-quinodimethanes and (1,1′-biphenyl)-4,4′-diylbis(diarylmethyl) compounds (*cf.* Thiele's and Chichibabin's hydrocarbons[22]) with the isoelectronic[7,8,10a] aminoborane $\overset{-}{B}=\overset{+}{N}$ function leads to electron-rich 1,4-bis(dimesitylboryl)-1,4-dihydropyrazine and 4,4′-bis(dimesitylboryl)-1,1′,4,4′-tetrahydro-4,4′-bipyridylidene,[10a] the radical cations of which (**3** and **4**) are isoelectronic with the radical anions **1** and **2**. In all cases **1**–**4**, the non-associated nature and the persistency can be ascribed to the steric protection of the sensitive B–N or B–C bonds by two mesityl groups which are known to screen effectively in a propeller–type conformation and restrict the coordination number of boron to three.[11]

The radical cations **3** and **4** are obtained *via* oxidation of neutral precursors using iodine in perchlorate-containing dichloromethane (**1**, $E_{\frac{1}{2}}$ = +0.20 V *vs.* ferrocene/ferrocinium) or the established[23] one-electron oxidant $AlCl_3/CH_2Cl_2$ (**4**, $E_{\frac{1}{2}}$ = −0.48 V *vs.* Fc/Fc$^+$). In comparison to similar species,[24,25] these potentials confirm the good π accepting properties of the dimesitylboryl substituent; the much lower $E_{\frac{1}{2}}$ value for the larger π system **4** relative to **3** indicates[9] a higher lying singly occupied molecular orbital (SOMO) which is in agreement with HMO/McLachlan calculation results (see below).

Although further electrochemical oxidation of the radical cations **3** and **4** proceeds irreversibly, the radical cations themselves are persistent enough to be studied by EPR/ENDOR spectroscopy (Fig. 5).

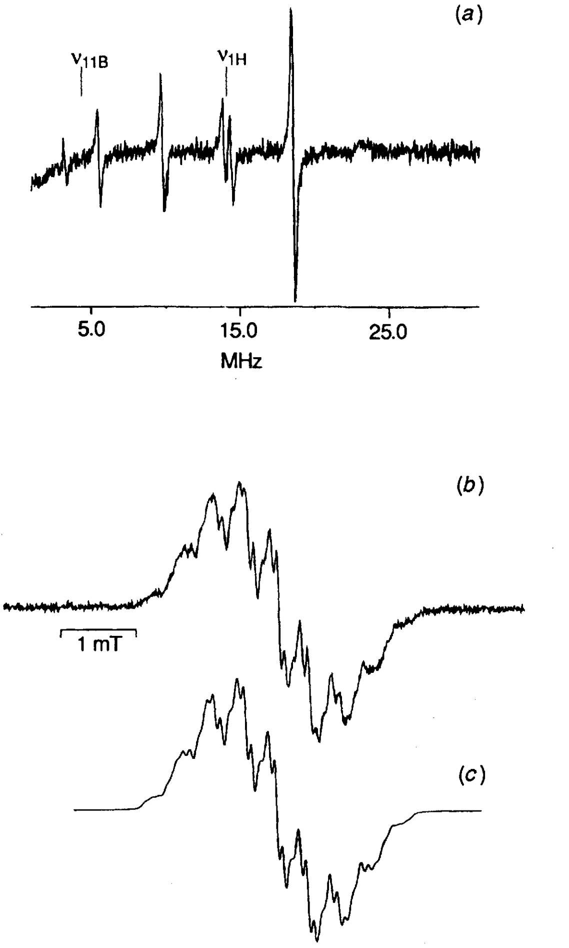


Fig. 5 ENDOR spectrum of cation radical **3** in dichloromethane (*a*, 190 K), EPR spectrum (*b*, 233 K) and its computer simulation (*c*) with the data from Table 1 and a line width of 0.10 mT

In contrast to the isoelectronic[10] radical anions **1** and **2**, the cations **3** and **4** exhibit ^1H *and* ^{11}B signals in their ENDOR spectra (Fig. 5). The ^{14}N hyperfine coupling constants could not be determined by ENDOR because of the inability to saturate at the higher temperatures necessary;[6] they were derived from simulations of sufficiently resolved EPR spectra (Fig. 5).

In comparison to related heterocyclic radical ions (see **5** and **6** in Table 1),[3,6,12,26] the ^1H hyperfine coupling constants indicate only little spin delocalization away from the CH π centres of the central pyrazine or 4,4′-bipyridine π systems. However, both the ^{11}B and the ^{14}N coupling constants are

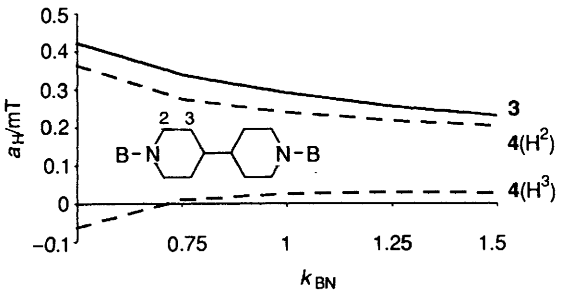
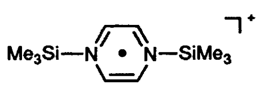


Fig. 6 Correlation of HMO/McLachlan-calculated ^1H coupling constants (Q_{CH} = 2.3 mT) with the overlap integral parameter k_{BN} for π systems **3** (——) and **4** (– – – –) ($h_B = -1.0$, $h_N = +1.0$; mesityl groups are neglected)

unusually small by comparison, *e.g.* the lowest hitherto reported value $a(^{14}N)$ = 0.664 mT of a 1,4-dihydropyrazine radical in **7**[26] is more than 50% higher than that of **3**. In a straightforward interpretation of these results, the unusually small heteroatom hyperfine splittings indicate a sizable π component within the $>\overset{-}{B}{=}\overset{+}{N}<$ (aminoborane) group because the electron spin–nuclear spin coupling constants reflect only spin density in s-type orbitals (Fermi contact term).[1] Compounds **3** and **4** thus confirm the significance of B–N π bonding by a method which reflects details of the electronic structure in a very sensitive manner. It is not surprising, therefore, that the otherwise extremely electron-rich 1,4-dihydropyrazine and 1,1′,4,4′-tetrahydro-1,1′-bipyridylidene π systems[26] are strongly stabilized owing to such B=N π bonding according to the *p*-quinonoid resonance forms **8** and **9**.



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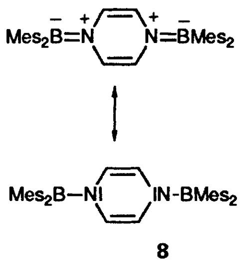

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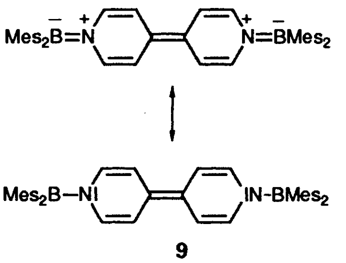

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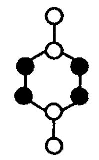
The smaller extent of spin delocalization to the periphery in the cations **3** and **4** relative to the isoelectronic species **1** and **2** is not only evident from the difference in ^{11}B coupling but also from the smaller mesityl proton hyperfine splitting in the cations (Table 1). As for **1** and **2**, the small hyperfine splitting from the various mesityl protons and the complicated pattern from the boron isotopes (Fig. 1) results in a large number of closely spaced theoretical lines ($>10^6$) which overlap to a large extent to cause rather poor resolution of the EPR spectra. The assignment 2-H > 3-H of the coupling constants in the 4,4′-bipyridine species **4** (Table 1) is based on HMO/McLachlan perturbation calculations (Fig. 6) which yield the best fit of calculated (Q = 2.3 mT) *vs.* experimental CH hyperfine splittings (Table 1) for k_{BN} = 1.0 with 0.288 mT (**3**) and 0.238 and 0.026 mT (**4**) as calculated coupling constants. The calculated McLachlan π spin populations at boron are 0.125 and 0.090 for **3** and **4**, respectively; small ^{11}B splittings at centres of high π spin density are not uncommon for boron-containing radicals.[27] Both the optimal value of k_{BN} = 1.0 and the assignment of the larger ^1H splitting to 2-H in **4** indicate[3] a rather strong π interaction between boron and nitrogen.[10]

As a remarkable corollary of these calculations we have found that the set of parameters $h_N = +1.0$, $h_B = -1.0$ and $k = 1.0$ produces a maximally delocalized SOMO for radical **3**, *i.e.* all eight (topologically inequivalent) π centres have equal π spin populations of 0.125 = 1/8.



$[R_3B(N\text{-}\pi\text{-}N)BR_3]^{\cdot-}$.—Boranes BR_3 with their empty p_z orbitals can serve as Lewis-acidic electrophiles towards heterocyclic bases and their anion radicals.[6] The resulting complexes with tetracoordinate boron should therefore undergo normal electron transfer at an electrode. The radical anion complexes **5** and **6** with two symmetrically coordinated boranes are related to the cation radicals **3** and **4** by a formal addition of two carbanions [eqn. (1)]; such carbanion exchange reactions of coordinatively active organometallics may be important for organic synthetic reactivity.[13] While mesityl groups are sterically too demanding to allow such an increase in the coordination number at boron, we can show here that cyclohexyl substituents in the radical anion **5c** still permit the formation of tetracoordinate boron.

$$[R_2B(N\text{-}\pi\text{-}N)BR_2]^{\cdot+} + 2\,R^- \rightleftharpoons [R_3B(N\text{-}\pi\text{-}N)BR_3]^{\cdot-} \quad (1)$$

Triethylborane radical species **5b** and **6** were described before in a detailed ENDOR study.[6] However, the ENDOR method does not permit a conclusive determination of the number of coupling nuclei and, hence, the composition (and charge) of the radical species. The alternative cationic formulation [eqn. (1)][12] to the anionic formulation **5** and **6** could not be ruled out definitely because the hyperfine coupling constants from the ethyl groups were too small to be detected by EPR spectroscopy[6,12] (which does allow a determination of the number of coupling nuclei). We have thus generated and studied the bis-adduct of volatile trimethylborane with reduced pyrazine (Fig. 7) in order to finally settle this question.[28]

The multinuclear (^1H, ^{11}B, ^{14}N) ENDOR spectrum of **5a** is similar to that of **5b**,[6] however, it reveals a rather large methyl proton coupling constant of *ca* 0.016 mT. The highly resolved EPR spectrum with $>10^4$ theoretical lines and a line width of 0.011 mT now allows us to determine the multiplicity of the methyl proton coupling; an optimal simulation of the experimental spectrum requires indeed 18 ^1H nuclei, *i.e.* six equivalent methyl groups, corresponding to the anionic formulation **5a**.

The larger ^{11}B and ^{14}N coupling constants of the anions **5** and **6**, in comparison to the cations **3** and **4**, indicate the absence of significant π bonding; instead, the dominating spin transfer mechanism is the spin polarization as in a typical 'ion pairs'.[29] We therefore assign the bipyridine proton splittings 2-H < 3-H of **6**[3,6] differently than those of **4** (Table 1).

The question of whether radical complexes such as **5** form *in situ* only after reduction of neutral mixtures (as do most radical ion pairs[29,30]) or if bis(borane) adducts $[R_3B(N\text{-}\pi\text{-}N)BR_3]$ are the predominant species from the beginning was addressed by studying the NMR-detectable[31,32] bis(triethylborane) adducts of pyrazine and 4,4′-bipyridine, *i.e.* the precursors of **5b** and **6** electrochemically in 1,2-dichloroethane. The compound with pyrazine ($E_{red} = -2.12$ V *vs.* SCE) is reduced reversibly to **5b** at a half-wave potential of −1.02 V, the complex $(Bp)[BEt_3]_2$ of the larger π system 4,4′-bipyridine (E_{red} =

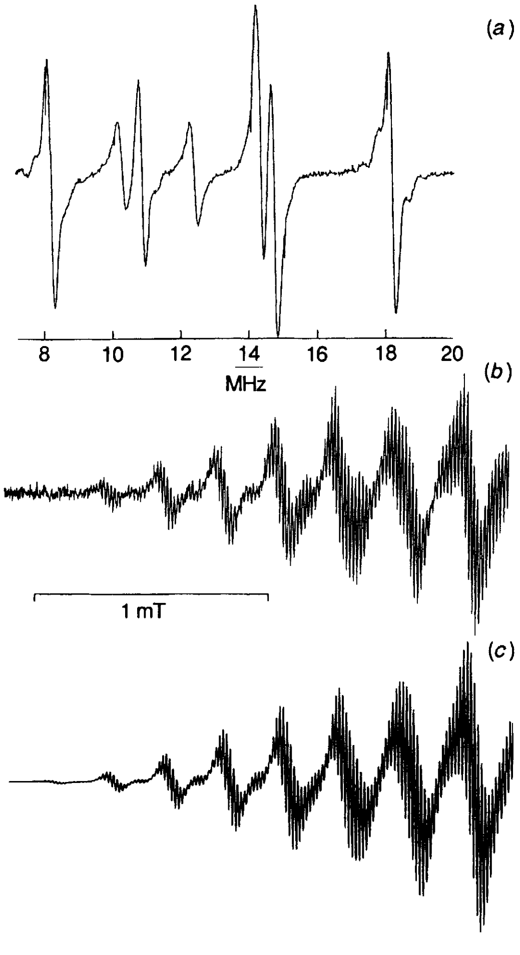


Fig. 7 ENDOR spectrum of radical anion **5a** in THF at 305 K (*a*) with one line at 8.2 MHz from ^{11}B coupling (ν_B = 4.78 MHz), one line pair from ^{14}N splitting (ν_N = 1.06 MHz) and two line pairs from ^1H coupling (ν_H = 14.55 MHz). Low-field section of the EPR spectrum (*b*, 300 K) and its computer simulation (*c*) with the data from Table 1 (18 methyl H) and a line width of 0.011 mT

– 1.80 V) is reduced less easily to **6** at – 1.26 V *vs.* SCE. Rather large peak potential separations of *ca.* 0.20 V at 100 mV s^{-1} point to complications in the heterogeneous electron transfer; nevertheless, the more facile reduction of the smaller bis(borane) adduct indicates a fairly large perturbation of the π systems[9] even by triorganoborane coordination to centres of high spin density.

Acknowledgements

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References

1 F. Gerson, *High Resolution ESR Spectroscopy*, Wiley/Verlag Chemie, London/Weinheim, 1970.
2 W. Kaim, *Chem. Ber.*, 1981, **114**, 3789.
3 W. Kaim, *J. Organomet. Chem.*, 1983, **241**, 157.
4 H. Bock and W. Fuss, *Z. Naturforsch., Teil B*, 1971, **26**, 525.
5 W. Kaim and A. Schulz, *Angew. Chem.*, 1984, **96**, 611; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 615.
6 W. Kaim and W. Lubitz, *Angew. Chem.*, 1983, **95**, 915; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 892; *Angew. Chem. Suppl.*, 1983, 1209.
7 A. Meller, *Gmelins Handbook of Inorganic Chemistry B 3rd Suppl., Vol 3*, 1988, p. 145–158.
8 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984; P. Fowler, *Nature*, 1992, **355**, 586.
9 A. Schulz and W. Kaim, *Chem. Ber.*, 1989, **122**, 1863.
10 (*a*) A. Lichtblau and W. Kaim, submitted to *Inorg. Chem*; (*b*) W. Kaim, *Angew. Chem.*, 1980, **92**, 940; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 911.
11 (*a*) R. A. Bartlett and P. P. Power, *Organometallics*, 1986, **5**, 1916; (*b*) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz and L.-T. Cheng, *J. Chem. Soc., Chem. Commun.*, 1990, 1489; (*c*) K. Okada, T. Sugawa and M. Oda, *J. Chem. Soc., Chem. Commun.*, 1992, 74.
12 W. Kaim, *Z. Naturforsch., Teil B*, 1981, **36**, 677.
13 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, 1991, **113**, 5606.
14 H. C. Brown and H. Peasall, *J. Am. Chem. Soc.*, 1945, **67**, 1765.
15 A. N. Nesmeyanov and R. A. Sokolik, *The Organic Compounds of Boron, Aluminium, Gallium, Indium and Thallium*, North-Holland Publishing Co., Amsterdam, 1967, p. 42.
16 E. Heilbronner and H. Bock, *The HMO-Model and its Application*, Wiley/Verlag Chemie, London/Weinheim, 1976.
17 A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
18 J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan and D. S. Miller, *J. Am. Chem. Soc.*, 1970, **92**, 6825.
19 R. G. Griffin and H. van Willigen, *J. Chem. Phys.*, 1972, **57**, 86.
20 M. Plato, W. Lubitz and K. Möbius, *J. Phys. Chem.*, 1981, **85**, 1202.
21 K. Grein, B. Kirste and H. Kurreck, *Chem. Ber.*, 1981, **114**, 254.
22 L. K. Montgomery, J. C. Huffman, E. A. Jurczak and M. P. Grendze, *J. Am. Chem. Soc.*, 1986, **108**, 6004.
23 H. Bock and W. Kaim, *Acc. Chem. Res.*, 1982, **15**, 9.
24 J. Baumgarten, C. Bessenbacher, W. Kaim and T. Stahl, *J. Am. Chem. Soc.*, 1989, **111**, 2126 and 5017.
25 S. Hünig and W. Schenk, *Liebigs Ann. Chem.*, 1979, 727. S. Hünig and H. Berneth, *Top. Curr. Chem.*, 1980, **92**, 1.
26 W. Kaim, *J. Am. Chem. Soc.*, 1983, **105**, 707. W. Kaim, *Rev. Chem. Intermed.*, 1987, **8**, 247.
27 H. Klusik and A. Berndt, *Angew. Chem.*, 1981, **93**, 903; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 870.
28 W. Kaim, *Acc. Chem. Res.*, 1985, **18**, 160.
29 J. H. Sharp and M. C. R. Symons, in *Ions and Ion Pairs in Organic Reactions*, ed. M. Szwarc, Wiley, New York, 1972, vol. 1, p. 177.
30 W. Kaim, in *Electron and Proton Transfer in Chemistry and Biology*, eds. A. Müller, E. Diemann, W. Junge and H. Ratajczak, Elsevier, Amsterdam, 1992, in the press.
31 H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 1974, **107**, 3070.
32 T. Stahl, Ph.D. Thesis, University of Stuttgart, 1992.

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